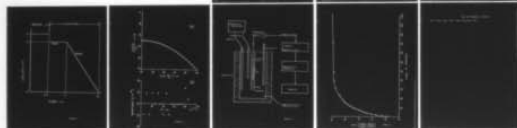AD-A041 211　　CATHOLIC UNIV OF AMERICA　WASHINGTON D C VITREOUS STA--ETC　F/G 20/12
THE THEORETICAL DEFINITION OF PARAMETERS TO PRODUCE GRADED INDE--ETC(U)
JUN 77　R K MOHR, P B MACEDO, T A LITOVITZ　　　N00019-76-C-0083

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This final report for FY-1976 presents the results of diffusion coefficient measurements for doping solutions in porous rods and results of a computer study done to determine values for the parameters necessary to produce a parabolic index profile by Molecular Stuffing.

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THE THEORETICAL DEFINITION OF PARAMETERS TO PRODUCE

GRADED INDEX PROFILES BY MOLECULAR STUFFING

Final Report: Contract N00019-76-C-0083

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I. INTRODUCTION

In previous reports the details of the Molecular Stuffing process have been discussed. Briefly, an alkali borosilicate glass is melted by conventional means, formed into rods, phase separated and leached to produce a porous structure which is then doped with an index modifier and sintered to yield a preform. An object of the research under this contract is to develop the ability to control the doping to produce a nearly parabolic index profile in the preform.

This final report for FY-1976 presents the results of diffusion coefficient measurements for doping solutions in porous rods and results of a computer study done to determine values for the parameters necessary to produce a parabolic index profile by Molecular Stuffing.

II PROGRESS IN THE DEVELOPMENT OF A STUFFING PROCEDURE TO PRODUCE PARABOLIC INDEX PROFILES

If one knows the composition profile (corresponding to the desired index-profile) it is possible to establish, for parabolic profiles, an unstuffing schedule which specifies the time variation of the concentration of the dopant compound solution at the surface of the rod. This is achieved by solving a diffusion equation which describes the isothermal kinetics of the desorption of $CsNO_3$ solution (inside the porous rod) for cylindrical geometry.

1.

The unstuffing (or desorption) schedule developed by computer study of the diffusion equation assumes a constant diffusion coefficient, D. This diffusion coefficient characterizes the inter-diffusion kinetics in the $CsNO_3$-H_2O system. We have observed that D is not a sensitive function of conentration, C, (in the temperature range of 0 to 100°C), but depends on the average pore size. It was necessary to determine how the diffusion coefficient depends on the average pore size. If the pore size dependence was not strong, then a large pore size variation could be accepted. On the other hand, a strong pore size dependence of D imposes strict demands on the pore size distribution of the porous glass, requiring it to be sharply peaked.

A computer study was instituted to solve the diffusion equations involved in the Molecular Stuffing process. The goal of this computer study was to discover an adequate unstuffing schedule for the development of parabolic profiles. Mathematically, the problem reduces to finding a proper time-dependent boundary condition which when combined with

(i) the diffusion equation, and

(ii) the uniform initial condition (t=0 corresponding to the end of the soaking step)

gives a parabolic profile as a solution. More precisely, let $C(r,t)$ be the concentration of $CsNO_3$ in solution at some point at a radial distance r from the axis of the rod and at a time t. Let b be the radius of the porous rod, then the initial condition corresponds to

$$c(r, t = 0) = c_o \, [0 \leqslant r \leqslant b] \qquad (1)$$

and the diffusion equation (as expressed in cylindrical geometry) is

$$\frac{\partial c}{\partial t} = D \ [\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \ \frac{\partial d}{\partial r}] \tag{2}$$

The problem is to specify the boundary condition $C(b,t)$ = ? so that the solution of (2) together with (1) and $C(b,t)$ will be parabolic after a certain time, t_f.

This formulation approximates a rod of finite length as an infinite cylinder which is a reasonable approximation since the ratio of length to diameter for our rods is gréater than 15. Another assumption employed in this formulation is that the porous rod soaked with $CsNO_3$ solution can be treated as a homogeneous cylinder of $CsNO_3$ solution where the effect of porosity is accounted for in the diffusion coefficient. It is difficult to justify this assumption a priori. However, results from experiments have shown reasonable agreement with the predictions of this formulation and support this assumption.

Carslaw and Jaegger have derived a solution of Eq. (2) corresponding to the initial condition (1) and an arbitrary boundary condition $C(b,t)$. The solution is in terms of an infinite series in which an integral of the type

$$\int_o^{t_f} e^{\alpha_n^2 \lambda} \ \phi \ (\lambda) \ d \ \lambda \quad [\text{where } c(b,t) \equiv \phi(t)]$$

appears as a coefficient of the nth term. It is not clear whether Carslaw and Jaegger's solution can be inverted analytically to derive the proper $\phi(t)$ for parabolic profiles. Since our primary interest in not in finding the particular boundary condition for

which the solution will be exactly parabolic, but is to discover
an adequate boundary condition which can be used in the laboratory
with relative ease, and for which the solution can be made as
parobolic as desired by adjusting the parameters. We decided to
solve this problem by using a computer. We have discovered an
unstuffing schedule $\phi(t)$, which gives nearly parabolic profiles.
These can be made parabolic to any desired degree of accuracy by
proper choice of parameters shown in Fig. 1. It shows $C(b,t)$ as
a function of unstuffing time. Time $t = 0$ marks the end of the
sorption step and the beginning of the unstuffing step. At the
end of the sorption stage, the rod has a uniform concentration of
$CsNO_3$ which we denote by C_0. The unstuffing schedule consists of
two steps:

(i) <u>hold</u>: the surface concentration $C(b,t)$ is held fixed at
   a certain value $C_1 (C_0)$ for a time, t_1

(ii) <u>ramp</u>: from time t_1 to t_f the surface concentration $C(b,t)$
   is decreased linearly so that

$$c(b,t) = C_1 [1-(\frac{t-t_1}{t_f-t_1})] \tag{3}$$

At the end ($t=t_f$) of unstuffing, the rod is quenched to a
lower temperature to freeze the profile.

The solution of the diffusion equation for these boundary
conditions can be written in terms of an infinite series:

$$C(r,t_f) = \sum_{n=1}^{\infty} \frac{8 \, J_0(\beta_n x)}{\beta^3 J_1(\beta_n)} \, \phi_n \tag{4}$$

where

$$\phi_n = \frac{e^{-\beta_n^2 \tau_f}}{4}\left[\theta e^{\beta_n^2 \tau_f} - e^{\beta_n^2 \tau_1} + \beta_n^2(C_0 - C_1)\right] \qquad (5)$$

$$x = r/b$$

$$J_0(\beta_n) = 0$$

$$\tau \equiv \frac{Dt}{b^2}, \quad \theta \equiv \frac{C_1}{\tau_f - \tau_1}$$

and J_0 and J_1 are Bessel's functions of zero and first order respectively. Notice that according to Eq. (4)

$$C(b, t_f) = 0$$

$$\text{and } C(0, t_f) = \sum_{n=1}^{\infty} \frac{8\,\phi_n}{\beta_n^3 J_1(\beta_n)}$$

Let ΔC be the difference between $C(0, t_f)$ and $C(b, t_f)$. Then

$$\Delta C = \sum_{n=1}^{\infty} \frac{8\,\phi_n}{\beta_n^3 J_1(\beta_n)} \qquad (6)$$

Notice that ΔC is a constant and is determined by four parameters, C_0, C_1, t_1 and t_f. Eq. (4) can now be rewritten in terms of ΔC as follows:

$$C(r, t_f) = \Delta C(1 - x^2) + \sum_{n=1}^{\infty} \frac{8 J_0(\beta_n x)}{\beta_n^3 J_1(\beta_n)}[\phi_n - \Delta C] \qquad (7)$$

Eq. (7) shows that the resulting profile $C(r, t_f)$ is parabolic provided the summation term is negligible. The higher order terms in the sum are indeed negligible since they contain in the denominator a factor of β_n^3 and β_n increases rapidly witn n. The first three terms in the sum can be made to vanish by choosing the three unknown parameters C_1, t_1 and t_f so that

$$\Delta C = \phi_1 = \phi_2 = \phi_3 \qquad (8)$$

Notice that C_0 is fixed by the soaking step. For those values
of C_1, t_1 and t_f which satisfy Eq. (8), Eq. (7) reduces to

$$C(r,t_f) = \Delta C \ (1-x^2) + \sum_{n=4} \frac{8J_0(\beta_n x)}{\beta^3 J(\beta_n)}[\phi_n - \Delta C] \qquad (9)$$

The assertion that the sum in Eq. (9) is negligible was verified
on the computer by actually summing up to 40 terms.

A typical simulation if Eq. (9) by keeping 40 terms in the
sum is shown in Fig. 2. This profile corresponds to the following
values of the parameters:

$C_0 = 0.03$, $b = 0.4$ cm, $D = 1 \times 10^{-5}$ cm^2/sec.

$C_1 = 0.0.4687$, $t_1 = 3917$ sec, $t_f = 4994$ sec.

Fig. 2 shows the normalized concentration $\frac{C(r,t_f)}{C_0}$ against normalized

radial distance $x(= r/b)$. The square points represent the solution
of Eq(9) and the curve represents a least square parabolic fit to
these points. The deviations, at any radius, are on the order of
10^{-8} as shown in Fig. 2(b). Thus it is clear that the unstuffing
schedule shown in Fig. 1 is adequate for producing parabolic pro-
files.

As mentioned above, the unstuffing schedule described in Fig.1
is adequate for parabolic profiling provided the diffusion coefficient
D is constant and uniform throughout the rod. D is the coefficient
of interdiffusion of, for example, $CsNO_3$-H_2O system inside the pores
of the porous glass. The constancy of D implies that it is indepen-
dent of concentration C of the solution. The uniformity of D demands,

on the other hand,   the uniformity of the pore size throughout the porous glass because D also depends on the pore size. We have carried out experiments to study

  (i) the concentration dependence of the diffusion coefficient D, and

 (ii) the uniformity of D along the axis of the rod.

The experimental technique to measure diffusion coefficients of solutions in the porous glass consists of monitoring the mass gain as a function of time of a porous glass rod at a fixed temperature in a $CsNO_3$ solution of fixed concentration.

A sketch of the apparatus is shown in Fig. 3. It consists of an aluminum block having the following features:

  (i) a vertical opening at the center, having a diameter of about 1 1/4" to hold a tight fitting glass tube containing a saturated solution of $CsNO_3$;

 (ii) two smaller openings to place a thermistor and a thermometer. The thermistor is connected to an external controller and is used to control the temperature of the block;

(iii) four heating elements at the corners which are connected to a power supply via the temperature controller. The temperature of the block is held constant to better than 0.01°C and is uniform to within 0.1°C.

The weight of the rod is monitored with the help of a transducer which converts mass variations into a voltage output. The transducer is accurate and sensitive to mass change on the order 10^{-4}g or larger.

It can be shown from diffusion theory that the time (t) variation of the mass (M) of the rod can be described by:

$$\frac{M(t) - M(0)}{M(\infty) - M(0)} = 1 - \sum_{n=1}^{\infty} \frac{4}{\beta^2_n} \; e^{-\left(\frac{Dt}{b^2} \beta^2_n\right)} \qquad (10)$$

where (i) β_n are the roots of the equation $J_0(\beta_n) = 0$ (J_0 being the Bessel function of zero order).

(ii) $M(0)$ and $M(\infty)$ are two constants representing the mass of the rod at the start ($t=0$) of the sorption process.

(iii) b is the radius of the rod.

Knowing $M(t)$ as a function of (t) it is possible to evaluate D by a non-linear least squares fit of Eq. (10) to the experimental data.

A typical measurement of $M(t)$ is shown in Fig. 4. The dots are the experimental data points and the curve is the non-linear least squares fit of Eq. (10). It is clear that the fit is ex-cellent. Therefore, we believe that this technique gives reliable estimates of the diffusion coefficients. The diffusion coefficients obtained in this fashion are average diffusion coefficients for the rod.

By using solutions of different concentrations, we measured diffusion coefficients as a function of concentration and found that D is relatively independent of concentration in the concentra-tion range of interest to us.

An experimental study of diffusion coefficient variation along the length of a 12" rod was carried out by dividing the rod into six 2" pieces and measuring the diffusion coefficient in each

piece.   Although the cross-section of the rod was not uniform along the length, the results were encouraging in the sense that the variation of D between different pieces was less than 2%.

III CONCLUSION

We have demonstrated by computer studies and by experiments that it is feasible to develop parabolic profiles in porous glass rods via molecular stuffing.   In particular for parabolic profiles, it is important to control the diffusion coefficient inside the pores to within 1%. This in turn requires a strict control of glass composition and heat-treatment.   We have shown by experiment that such a control is possible.

CAPTIONS

Figure 1. Unstuffing schedule for parabolic profiling by molecular stuffing. Time t = 0 marks the end of soaking and the beginning of unstuffing (or desorption) stage.

Figure 2. (a) A plot of normalized concentration $\frac{C(r)}{CO}$ vs. normalized radius x (=r/b). The squares represent the solutions of Eq. (9) and the curve represents a least squares parabolic fit to the square points.

(b) The deviation between square points and parabola are shown as a function of x.

Figure 3. A sketch of the apparatus to measure diffusion coefficient of $CsNO_3$-H_2O system inside the porous rods.

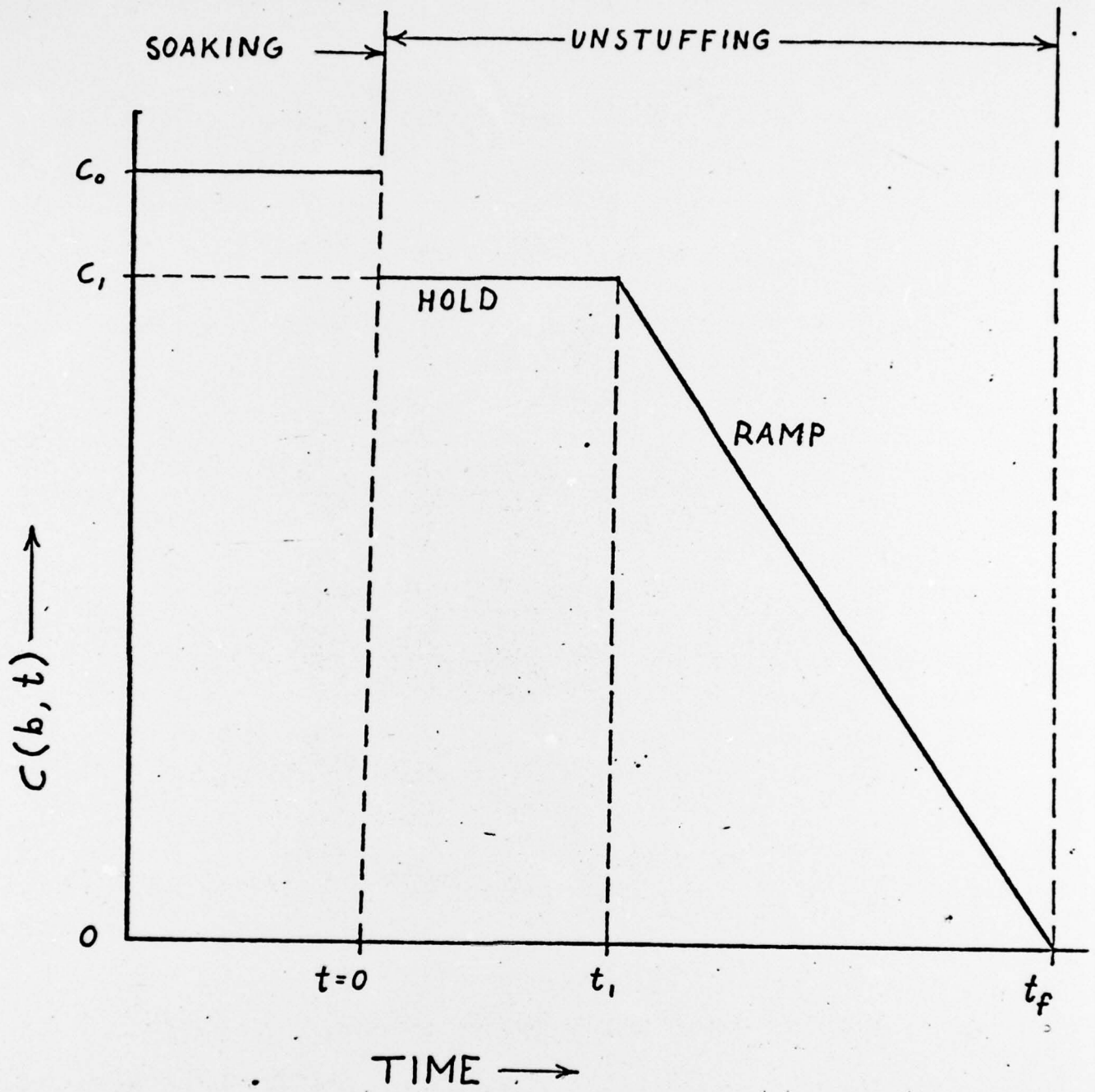Figure 4. A typical measurement of mass change M(t) as a function of time t. The dots represent experimental data and the curve is a non-linear least squares fit of Eq.(10).
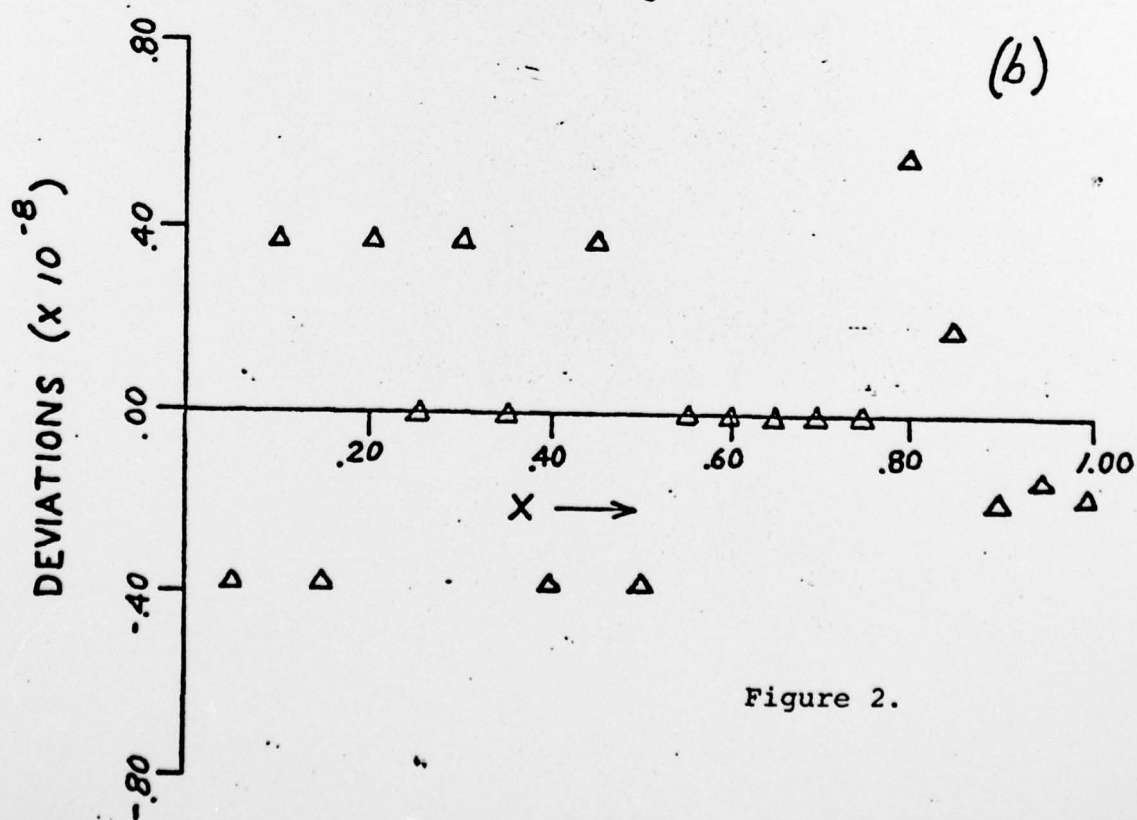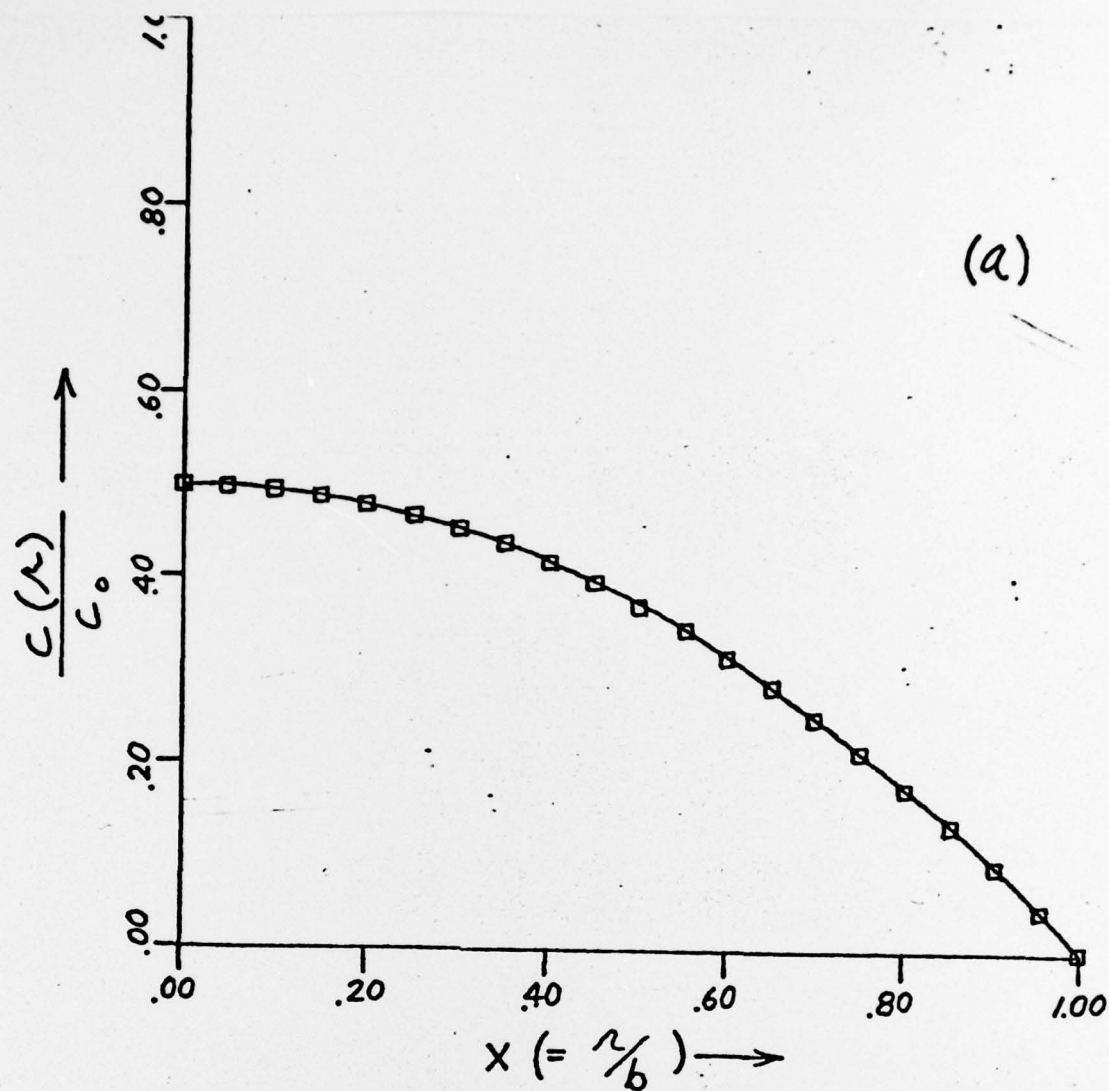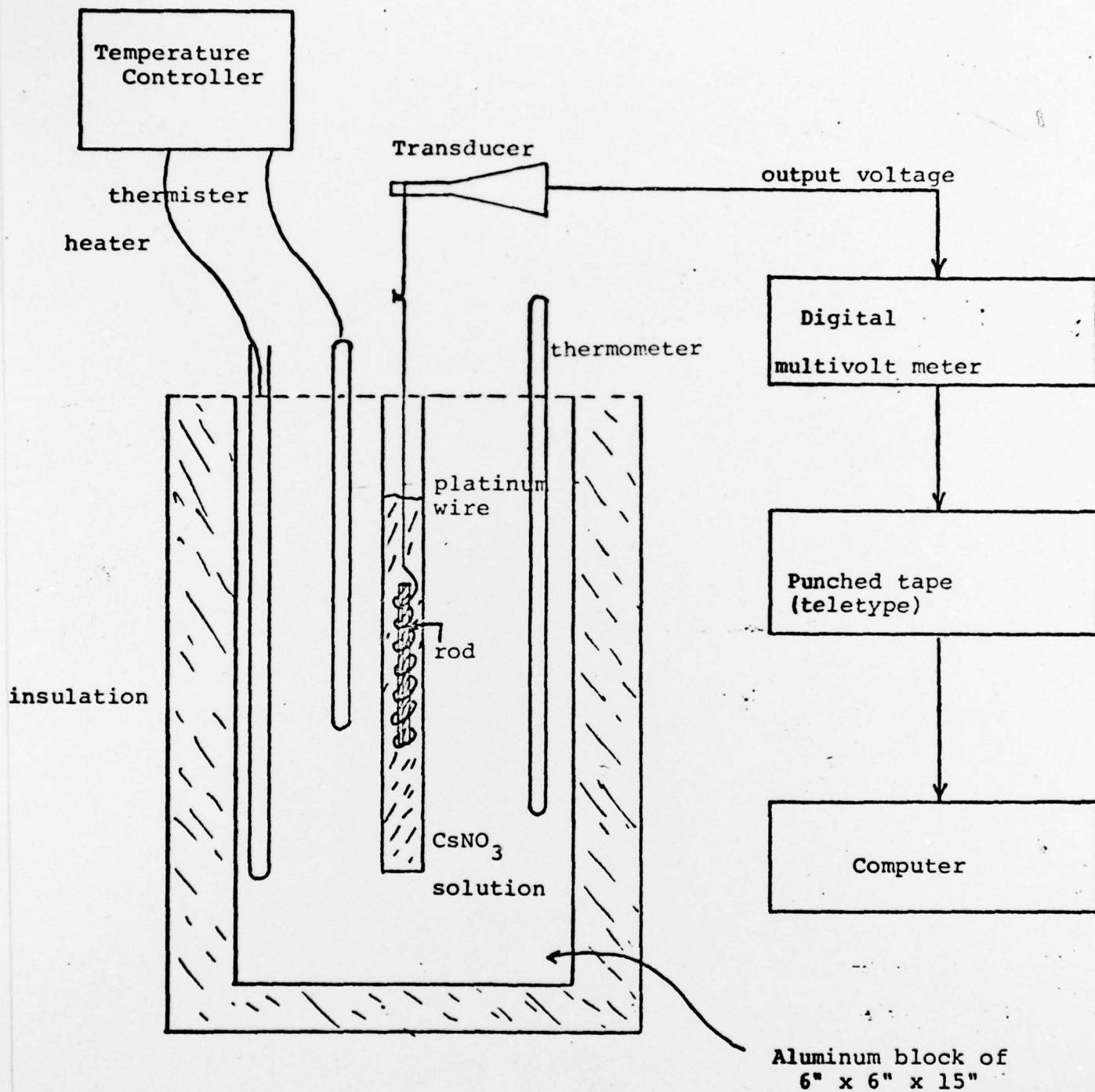
Figure 1.

Figure 2.

Figure 3.

Figure 4.

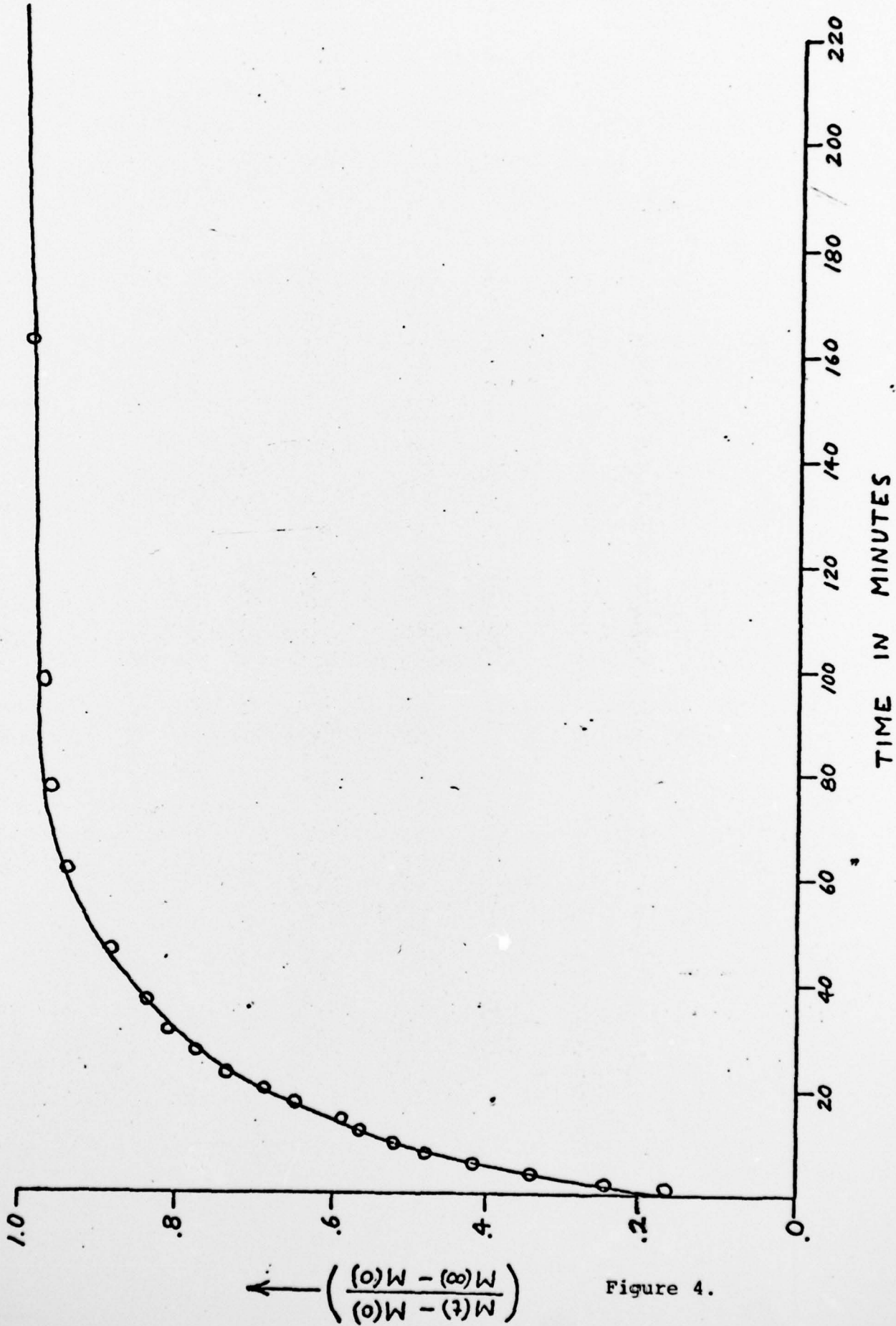$$\left(\frac{M(t) - M(\infty)}{M(0) - M(\infty)} \right) \longleftarrow$$

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